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(54) Title: METAL ALKOXIDE HYDROLYTIC POLYCONDENSATION SOLUTION AND TRANSPARENT FILMS MANU-
FACTURED THEREFROM

(57) Abstract: A hydrolysis polycondensation product solution comprising a hydrolysis-polycondensation product of an aluminum alkoxide represented by the formula $Al(OR)_3$ (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino) which cures within 24 hours at a temperature of about 10 to about 40°C, to thereby form a transparent film; a method for producing an aluminum alkoxide hydrolysis polycondensation product solution, comprising adding an aluminum alkoxide represented by the formula $Al(OR)_3$ in an amount of about 1 mole part into a mixed solution of about 0.1 to about 3 mole parts of (-diketone, about 0.5 to about 2 mole parts of an acid and about 10 to about 20 mole parts of an alcohol; adding about 30 mole parts or more of water to the solution, per 1 mole part of the aluminum alkoxide; and heating the solution to a temperature of about 40 to about 70°C; and a similar method for producing an aluminum alkoxide-titanium alkoxide cohydrolysis polycondensation product solution is also provided.

WO 2004/014986 A1

DESCRIPTION

METAL ALKOXIDE HYDROLYTIC POLYCONDENSATION SOLUTION AND TRANSPARENT FILMS
MANUFACTURED THEREFROM

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Cross Reference to Related Application

This application is an application filed under 35
U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C.
§119(e)(1) of the filing date of the Provisional
10 Application No. 60/403,474 filed on August 15, 2002, and
No. 60/437,318 filed on January 2, 2003, pursuant to 35
U.S.C. §111(b).

Field of the Invention

The present invention relates to a product which is
15 obtained through hydrolysis and polycondensation of an
aluminum alkoxide and which is capable of forming a
transparent and highly durable film (hereinafter the
product may be referred to simply as an "aluminum
alkoxide hydrolysis-polycondensation product") or a
20 product which is obtained through cohydrolysis and
polycondensation of an aluminum alkoxide and a titanium
alkoxide and which is capable of forming a transparent
and highly durable film (hereinafter the product may be
referred to simply as an "aluminum alkoxide-titanium
25 alkoxide cohydrolysis-polycondensation product"); a
method for producing any of the products; a composition
for forming a photocatalytic film, containing any of the
products and photocatalytic particles; and a composite
material, incorporating the thus-formed film, which
30 exhibits useful properties including deodorization,
antifouling, hydrophilic, and antibacterial effects.

Background Art

Conventionally, in order to enhance durability of
concrete products or iron and steel products, there have
35 been proposed techniques for applying, onto the surface
of such a product, a coating agent containing a
hydrolysis product of an alkoxide of a metal (e.g.,

silicon, zirconium, or titanium), the agent being capable of forming a highly durable film (e.g., Japanese Patent Application Laid-Open (kokai) Nos. 2-69375 and 62-36045). However, the above techniques involve problems, in that
5 film formation requires heating and the thus-formed film is not transparent.

Meanwhile, there have been proposed photocatalytic semiconductors which generate, through photoexcitation, active oxygen species exhibiting strong oxidation power.
10 Since most organic substances are decomposed by means of the oxidizing effect (i.e., photocatalytic effect) of the active oxygen species, such a photocatalytic semiconductor has been employed in various articles for decomposition of malodorous substances, prevention of
15 contamination with organic substances, and antibacterial purposes. The photocatalytic semiconductor exhibits the photocatalytic effect at its surface, and therefore, the semiconductor must be provided on the surface of a member requiring photocatalytic activity. In general, the
20 photocatalytic semiconductor is provided on the surface of such a member by means of a simple process; specifically, a process in which the semiconductor is mixed with a binder, and the resultant mixture is applied onto the member. When an organic polymer serving as a
25 binder is employed in combination with the photocatalytic semiconductor, the binder is oxidized and decomposed because of the photocatalytic effect, raising the need for employment of a binder which is not easily decomposed (e.g., a fluorine resin binder or a silicone resin
30 binder) (Japanese Patent Nos. 2756474 and 3027739).

However, when photocatalytic semiconductor particles are incorporated into such a resin binder, the surfaces of the particles are coated with the binder, leading to problems that the binder blocks light or substances to be
35 decomposed from reaching the particles, and lowers the photocatalytic effect of the particles. Also, employment of such a resin binder involves a problem that the resin

must be cured through heating.

Japanese Patent Application Laid-Open (*kokai*) No. 8-164334 discloses a process employing, as a binder, an alkyl silicate condensation product of relatively low molecular weight obtained through hydrolysis of a hydrolytic silicon compound. In this process, the binder can be cured at a low temperature, and lowering of the photocatalytic effect is suppressed.

However, in this process, hydrolysis must be performed at a pH of 4 or less or under alkaline conditions, and thus a solution containing the binder and photocatalytic particles, which is to be applied to a substrate, has acidity or alkalinity when the solution is applied to a corrosion-prone substrate such as iron or aluminum, the application method must be modified. Meanwhile, the aforementioned condensation product fails to be employed as a binder in a neutral titanium oxide sol.

Japanese Patent Application Laid-Open (*kokai*) No. 9-40872 discloses a process employing a hydrolytic organometallic compound as a binder. However, this process involves problems in that hydrolysis of the compound is insufficiently regulated, and a titanium oxide sol aggregates and exhibits low storage stability.

As aluminum alkoxide is very readily hydrolyzed by water in the presence of a small amount of a catalyst, a neutral sol can be formed from aluminum alkoxide. However, difficulty is encountered in forming a transparent and highly durable film from the sol, and the sol has a very short pot life. Meanwhile, Japanese Patent Application Laid-Open (*kokai*) No. 7-216552 discloses a technique for forming a highly durable film, but this technique involves problems in that a coupling agent which causes impairment of the film must be employed, and curing of the film requires heating.

A photocatalyst requires a binder which has a long pot life, which is not impaired by the photocatalyst, and

which enables formation of a transparent and highly stable film.

Objects of the present invention are to provide a hydrolysis-polycondensation product which is stable and tractable; a hydrolysis-polycondensation product solution which enables, through drying (but without heating), formation of a transparent and highly durable film on the surface of a substrate, and which, when hermetically sealed, can be stored at ambient temperature over a long period of time; a composition for forming a photocatalytic film, containing the hydrolysis-polycondensation product solution and photocatalytic semiconductor particles; and a composite material formed from the composition.

Summary of the Invention

In order to attain the aforementioned objects, the present invention provides the following.

[1] A hydrolysis polycondensation product solution, comprising a hydrolysis-polycondensation product of an aluminum alkoxide represented by the formula $Al(OR)_3$, (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino); an alcohol; and water, which composition cures within about 24 hours at a temperature of about 10 to about 40°C, to thereby form a transparent film.

[2] A hydrolysis polycondensation product solution, comprising a cohydrolysis-polycondensation product of an aluminum alkoxide represented by the formula $Al(OR)_3$, (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino) and a titanium alkoxide represented by the formula

Ti(OR')₄ (wherein R' represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino); an alcohol; and water, which composition cures within about 24 hours at a temperature of about 10 to about 40°C, to thereby form a transparent film.

[3] A hydrolysis polycondensation product solution according to [1] or [2] above, comprising β-diketone.

[4] An aluminum alkoxide hydrolysis-polycondensation product solution comprising an aluminum alkoxide represented by the formula Al(OR)₃ (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino), a β-diketone, an acid, water, and an alcohol in proportions by mol of about 1 : about 0.1 to about 3 : about 0.5 to about 2 : at least about 30 : about 10 to about 20.

[5] An aluminum alkoxide hydrolysis-polycondensation product solution comprising an aluminum alkoxide represented by the formula Al(OR)₃ (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino), a titanium alkoxide, a β-diketone, an acid, water, and an alcohol in proportions by mol of about 1 : about 0.01 to about 0.5 : about 0.1 to about 3 : about 0.5 to about 2 : about 1 to about 20 : about 80 to about 140.

[6] A hydrolysis-polycondensation product solution according to any one of [3] or [5] above, wherein the β-

diketone is acetylacetone, the acid is acetic acid, and the alcohol is methanol.

[7] A hydrolysis-polycondensation product solution according to [4] above, which has a kinematic viscosity of about 1.5×10^{-6} to about 3.0×10^{-6} m²/s.

[8] A hydrolysis-polycondensation product solution according to [5] above, which has a kinematic viscosity of about 0.5×10^{-6} to about 2.0×10^{-6} m²/s.

[9] A hydrolysis-polycondensation product solution according to any one of [1] through [8] above, which, when hermetically stored at about 20°C for about 90 days, undergoes no change in kinematic viscosity, and which, even when mixed with photocatalytic particles, does not cause cohesion of the particles.

[10] A hydrolysis-polycondensation product solution according to any one of [1] to [9] above, wherein a powder formed through drying of the hydrolysis-polycondensation product solution at about 200°C has a specific surface area of at least about 100 m²/g.

[11] A hydrolysis-polycondensation product solution according to any one of [1] to [10] above, wherein, when a film is formed through drying of the hydrolysis-polycondensation product solution at about 40°C so as to have a thickness of about 200 nm, the film has a total light transmittance of at least about 95% and a haze of about 1% or less.

[12] A method for producing an aluminum alkoxide hydrolysis polycondensation product solution, comprising adding an aluminum alkoxide represented by the formula Al(OR)_3 (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino) in an amount of about 1 mole part into a mixed solution of about 0.1 to about 3 mole parts

of β -diketone, about 0.5 to about 2 mole parts of an acid and about 10 to about 20 mole parts of an alcohol; adding about 30 mole parts or more of water to the solution, per 1 mole part of the aluminum alkoxide; and heating the solution to a temperature of about 40 to about 70°C.

[13] A method for producing an aluminum alkoxide-titanium alkoxide cohydrolysis polycondensation product solution, comprising adding an aluminum alkoxide represented by the formula $\text{Al}(\text{OR})_3$ (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino) in an amount of about 1 mole part into a mixed solution of about 0.1 to about 3 mole parts of β -diketone, about 0.5 to about 2 mole parts of an acid, about 80 to about 140 mole parts of an alcohol and about 1 to about 20 mole parts of water; and adding to the solution about 0.01 to about 0.5 mole part of a titanium alkoxide represented by the formula $\text{Ti}(\text{OR}')_3$ (wherein R' represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino), per 1 mole part of the aluminum alkoxide, while heating the solution to a temperature of about 40 to about 70°C.

[14] A composition for forming a photocatalytic film, comprising the hydrolysis-polycondensation product solution as recited in [1] through [11] above, and photocatalytic particles exhibiting, through photoexcitation, deodorization, antifouling, hydrophilic, and antibacterial effects.

[15] A composition for forming a photocatalytic film according to [14] above, wherein the solid content of the

photocatalytic particles is about 0.5 mass% to about 7 mass%, and the amount of the hydrolysis-polycondensation product of an aluminum alkoxide represented by the formula Al(OR)_3 is about 0.5 mass% to about 10 mass% as reduced to Al_2O_3 .

[16] A composition for forming a photocatalytic film according to [14] above, wherein the solid content of the photocatalytic particles is about 0.5 mass% to about 7 mass%, and the amount of the aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product is about 0.1 mass% to about 3 mass% as reduced to Al_2O_3 and about 0.1 mass% to about 1 mass% as reduced to TiO_2 .

[17] A composition for forming a photocatalytic film according to any one of [14] through [16] above, wherein the photocatalytic particles have an average particle size of about 0.001 to about 0.1 μm as calculated from the BET specific surface area.

[18] A composition for forming a photocatalytic film according to any one of [14] through [17] above, wherein the photocatalytic particles contain at least one species selected from the group consisting of titanium dioxide particles and titanium dioxide particles having a condensed phosphate on their surfaces.

[19] A composition for forming a photocatalytic film according to [18] above, wherein the titanium dioxide particles contain at least one crystal form selected from the group consisting of rutile, anatase, and brookite.

[20] A composition for forming a photocatalytic film according to any one of [14] through [19] above, wherein the content of the alcohol is about 30 mass% or less.

[21] A composition for forming a photocatalytic film according to any one of [14] through [20] above, which has a pH of about 5 to about 8.

[22] A composite material comprising a film exhibiting, through photoexcitation, deodorization, antifouling, hydrophilic, and antibacterial effects, the film being formed from a composition for forming a photocatalytic

film, the composition containing an aluminum alkoxide hydrolysis-polycondensation product solution or an aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product solution and photocatalytic particles.

[23] A composite material according to [22] above, wherein the photocatalytic particles are at least one species selected from the group consisting of titanium dioxide particles and titanium dioxide particles having a condensed phosphate on their surfaces.

[24] A composite material according to [23] above, wherein the titanium dioxide particles contain at least one crystal form selected from the group consisting of rutile, anatase, and brookite.

[25] A composite material according to any one of [22] to [24] above, wherein, after the material is photoexcited such that the contact angle between the film and water becomes about 10° or less, and then the material is allowed to stand in the dark for about 48 hours, the contact angle between the film and water is about 10° or less.

[26] A composite material according to any one of [22] through [25] above, wherein, after the material is subjected to an acceleration-exposure test employing a xenon lamp for about 5,000 hours, the film has a pencil hardness value of at least about 2H.

[27] A composite material according to any one of [22] through [26] above, wherein, when the thickness of the film is about 200 nm, the film has a total light transmittance of at least about 90% and a haze of about 1% or less.

[28] A material for an exterior wall of a building, a soundproof wall for a road, a windowpane of a building, a glass material for a showcase, a glass material for a fluorescent lamp, a guardrail, a filter for a deodorizing apparatus, a reactor for water treatment, an interior decoration tile, a water bath, or a shade for a lighting

apparatus, comprising a composite material as recited in any one of [22] through [27] above.

[29] An advertising signboard, a transparent soundproof wall for a road, a transparent resin building material
5 for exterior finishing, or a shade for a lighting apparatus, comprising a hard coat layer containing a composite material as recited in any one of [22] through [28] above.

The present inventors have found that particularly
10 when a film is formed from an aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product, the adhesive strength between the film and a substrate is enhanced. The present invention has been accomplished on the basis of this finding.

15 Modes for Carrying Out the Invention

The composition for forming a film contains a product obtained through hydrolysis and polycondensation of an aluminum alkoxide represented by the formula Al(OR)_3 (wherein R represents a substituted or
20 unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino) or a product obtained through
25 cohydrolysis and polycondensation of the aluminum alkoxide and a titanium alkoxide. By mixing the composition, i.e., the hydrolysis polycondensation product solution with photocatalytic particles (in this case, the composition serves as a binder), the resultant
30 mixture is employed as a composition for forming a photocatalytic film.

In the aluminum alkoxide represented by the formula Al(OR)_3 , "R" is not limited, however, examples of "R" include a substituted or unsubstituted, straight or
35 branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group. The hydrocarbon of these groups may optionally contain at least one from the group

consisting of carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino. The number of carbon may preferably be 1 to 48 in the aluminum alkoxide. Of these, 1 to 24 is preferred, 3 to 12 is more preferred.
5 (R is most preferably C1-C4 alkyl group.)

Preferred examples of the aluminum alkoxide include aluminum trimethoxide, aluminum triethoxide, aluminum tripropoxide, and aluminum tributoxide. Aluminum triisopropoxide and aluminum trimethoxide are more
10 preferred.

In the titanium alkoxide represented by the formula $Ti(OR')_4$, "R'" is not limited, however, examples of "R'" include a substituted or unsubstituted, straight or branched, saturated or unsaturated, alkyl group, alkyl-
15 ester group or aryl group. The hydrocarbon of these groups may optionally contain at least one from the group consisting of carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino. The number of carbon may preferably be 1 to 64 in the titanium alkoxide. Of these
20 1 to 32 is preferred, 4 to 16 is more preferred. (R' is most preferably C1-C4 alkyl group.)

Examples of the titanium alkoxide include titanium tetraethoxide, titanium tetraisopropoxide, and titanium tetra-n-butoxide. Titanium tetraethoxide and titanium
25 tetraisopropoxide are preferred.

When such an aluminum alkoxide or titanium alkoxide is hydrolyzed, an acid is required to coexist with the alkoxide. The acid may be an inorganic acid or an organic acid. The inorganic acid is preferably
30 hydrochloric acid, nitric acid, or sulfuric acid and, more preferably, is nitric acid. The organic acid is preferably formic acid, acetic acid, propionic acid, or butanoic acid, most preferably acetic acid. The inorganic acid and the organic acid may be employed in
35 combination.

In order to suppress hydrolysis of the alkoxide to some extent, thereby regulating the polymerization

degree, addition of a β -diketone is required. Since a β -diketone forms a stable complex with a hydrolysis product to thereby prevent generation of precipitates, the β -diketone contributes to enhancement of long-term stability of the aluminum alkoxide hydrolysis-polycondensation product or the aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product.

Examples of the β -diketone include acetylacetone, 2,4-hexanedione, 2,4-heptanedione, 3,5-heptanedione, and 2,4-octanedione. Of these, acetylacetone is preferred.

Hydrolysis of the aluminum alkoxide or the titanium alkoxide requires water. The water to be employed may be tap water, ion exchange water, or distilled water. Of these, ion exchange water or distilled water, which does not contain excess ions causing storage instability, is preferred.

An alcohol serving as a solvent is required for regulating the concentration of the aluminum alkoxide or the titanium alkoxide and for controlling the amount of the alkoxide to be hydrolyzed. The alcohol employed as an organic solvent in the present invention is a hydrophilic alcohol having compatibility with water, which is required for hydrolysis. Preferred examples of the alcohol include methanol, ethanol, 1-propanol, 2-propanol, and denatured alcohol containing a mixture thereof. Of these, methanol is more preferred, from the viewpoint of stability.

The aforementioned constitutive components are critical from the viewpoints of adhesive strength of the film and stability of the hydrolysis-polycondensation product solution. The amount of the aluminum alkoxide hydrolysis-polycondensation product in the solution in which the product is dispersed is about 0.5 to about 10 mass%, preferably about 1 mass% to about 5 mass% more preferably about 2 mass% to 4 mass% as reduced to Al_2O_3 . The amount of the aluminum alkoxide-titanium alkoxide

cohydrolysis-polycondensation product in the solution in which the product is dispersed is about 0.5 mass% to about 10 mass% more preferably about 1 mass% to 5 mass%, most preferably about 2 mass% to 4 mass% as reduced to Al_2O_3 , and about 0.1 mass% to about 3 mass% more preferably about 0.3 mass% to 2.7 mass% most preferably about 0.5 mass% to 2.5 mass% as reduced to TiO_2 . When the amount of the aluminum alkoxide hydrolysis-polycondensation product as reduced to Al_2O_3 is less than about 0.5 mass%, the amount of the solution must be increased to obtain a predetermined adhesive strength, leading to problems in that, for example, the other components of the composition are reduced. In contrast, when the amount of the aluminum alkoxide hydrolysis-polycondensation product as reduced to Al_2O_3 exceeds about 10 mass%, the solution becomes unstable, and precipitates tend to be generated. When the amount of the aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product as reduced to TiO_2 is less than about 0.1 mass%, hydrolysis of the aluminum alkoxide does not proceed, whereas when the amount of the product as reduced to TiO_2 exceeds about 3 mass%, polymerization proceeds excessively, and precipitates tend to generate. Herein, for the sake of convenience, the amount of the hydrolysis-polycondensation product as reduced to Al_2O_3 is represented by the Al content of the product as reduced to Al_2O_3 , and the amount of the cohydrolysis-polycondensation product as reduced to TiO_2 is represented by the Ti content of the product as reduced to TiO_2 . In this case, the mole number of Al_2O_3 is 1/2 that of Al contained in the aluminum alkoxide hydrolysis-polycondensation product, and the mole number of TiO_2 is equal to that of Ti contained in the titanium alkoxide cohydrolysis-polycondensation product.

35 The required amount of the β -diketone is about 0.1 mol to about 3 mol, preferably about 0.7 to about 2.9 mol, more preferably about 1 to about 2.9 mol on the

basis of 1 mol of the aluminum alkoxide. When the amount of the β -diketone is less than about 0.1 mol, stability of the solution is lowered, whereas when the amount exceeds about 3 mol, curing of the film requires long time and high temperature.

The amount of the acid when used is preferably about 0.5 mol to about 2 mol more preferably about 0.6 to about 1.8 mol, most preferably 0.8 mol to 1.5 mol on the basis of 1 mol of the aluminum alkoxide. When the amount of the acid is less than about 0.5 mol, hydrolysis and polycondensation proceed insufficiently, resulting in poor adhesion of the solution, whereas when the amount exceeds about 2 mol, the pH of the solution becomes lower than about 5 which is not desirable.

The amount of water required for hydrolysis of the aluminum alkoxide differs from that of water required for cohydrolysis of the aluminum alkoxide and the titanium alkoxide.

In the case of hydrolysis of the aluminum alkoxide, the amount of water is preferably about 30 mol or more preferably about 40 mol or most preferably about 50 mol or more on the basis of 1 mol of the aluminum alkoxide. This is because, when the amount of water is less than about 30 mol, the powdery aluminum alkoxide dissolves in water incompletely, leading to insufficient hydrolysis. In the case of cohydrolysis of the aluminum alkoxide and the titanium alkoxide, the amount of water is preferably about 1 to about 20 mol, more preferably about 1 to about 15 mol, most preferably about 1 to about 10 mol on the basis of 1 mol of the aluminum alkoxide. This is because, when the amount of water is less than about 1 mol, hydrolysis fails to proceed, whereas when the amount of water exceeds about 20 mol, the pot life of the solution is shortened.

Also, the amount of the alcohol required for hydrolysis of the aluminum alkoxide differs from that of the alcohol required for cohydrolysis of the aluminum

alkoxide and the titanium alkoxide. In the case of hydrolysis of the aluminum alkoxide, the amount of the alcohol is preferably about 10 mol to about 20 mol, more preferably about 11 mol to about 19 mol on the basis of 1 mol of the aluminum alkoxide. When the amount of the alcohol is less than about 10 mol, the storage stability of the solution is impaired, whereas when the amount of the alcohol exceeds about 20 mol, a large amount of the alcohol volatilizes in the environment during the course of application of the solution. In the case of cohydrolysis of the aluminum alkoxide and the titanium alkoxide, the amount of the alcohol is preferably about 80 to about 140 mol, more preferably about 30 mol to about 120 mol on the basis of 1 mol of the aluminum alkoxide. When the amount of the alcohol is less than about 80 mol, polycondensation proceeds excessively, and the resultant solution fails to exhibit high adhesive strength, whereas when the amount of the alcohol exceeds about 140 mol, the amount of the hydrolysis-polycondensation product in the solution decreases, and the solution becomes unsuitable for practical use.

When the hydrolysis-polycondensation product solution is prepared from the aforementioned components, all the components may be mixed together at once. However, preferably, the solution is prepared through the following procedure: firstly the aluminum alkoxide is dissolved in a mixture of the alcohol (i.e., a hydrophilic organic solvent), the β -diketone, and the acid; and subsequently water is added to the resultant mixture. When cohydrolysis of the aluminum alkoxide and the titanium alkoxide is performed, the titanium alkoxide must be added to the mixture in the final procedure. In the case of the cohydrolysis, the titanium alkoxide may be a mixture of titanium alkoxide, alcohol, β -diketone, and an acid.

After completion of mixing, the resultant mixture is

preferably reacted at a temperature of about 40°C to about 70°C under reflux in order to prevent evaporation of low-temperature volatile components. When the reaction temperature is lower than about 40°C, the aluminum alkoxide is incompletely dissolved in the mixture, and hydrolysis proceeds insufficiently. In contrast, when the reaction temperature is higher than about 70°C, hydrolysis proceeds excessively, and sol precipitates are generated. The reaction (heating) time is preferably about 20 minutes to two hours. When the heating time is shorter than about 20 minutes, hydrolysis and polycondensation of the aluminum alkoxide proceed insufficiently, whereas when the heating time is longer than two hours, hydrolysis and polycondensation proceed excessively, leading to low adhesive strength of the resultant solution.

Hereinafter, the thus-prepared hydrolysis-polycondensation product solution may be referred to as the "binder solution."

When the aluminum alkoxide hydrolysis-polycondensation product solution serves as the binder solution, the kinematic viscosity of the binder solution is preferably regulated to about 1.5×10^{-6} to about 3.0×10^{-6} m²/s, more preferably about 1.6×10^{-6} m²/s to about 3.0×10^{-6} m²/s, most preferably about 1.6×10^{-6} to about 2.9×10^{-6} m²/s. Meanwhile, when the aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product solution serves as the binder solution, the kinematic viscosity of the binder solution is preferably regulated to about 0.5×10^{-6} to about 2.0×10^{-6} m²/s, more preferably about 0.7×10^{-6} to about 1.9×10^{-6} m²/s, most preferably about 1.0×10^{-6} to about 1.8×10^{-6} m²/s. When the former and latter binder solutions have kinematic viscosities of lower than about 1.5×10^{-6} m²/s and about 0.5×10^{-6} m²/s, respectively, hydrolysis and

polycondensation proceed insufficiently, whereas when the former and latter binder solutions have kinematic viscosities of higher than about 3.0×10^{-6} m²/s and about 2.0×10^{-6} m²/s, respectively, polycondensation proceeds
5 excessively and the solutions become unstable, leading to generation of precipitates. The above-prepared aluminum alkoxide polycondensation product solution (binder solution), when hermetically stored at about 20°C for about 90 days, undergoes no change in kinematic
10 viscosity, and, even when mixed with photocatalytic particles, does not cause cohesion of the particles.

Without being subjected to any treatment, the solution can be employed as a composition for forming a transparent film which can impart durability to a
15 substrate (e.g., iron and steel, or concrete); specifically, a transparent film which can prevent iron and steel from rusting or prevent concrete from cracking.

When the binder solution is applied onto a substrate and then dried (for example, at about 10 to about 40°C),
20 a transparent film is formed. When the film is formed through curing so as to have a thickness of 200 nm, the film has a total light transmittance of about 95% or more. When the total light transmittance is lower than about 95%, the film exhibits poor transparency, spoiling
25 the design of the substrate.

When the binder solution is mixed with photocatalytic particles, a composition for forming a photocatalytic film is prepared (hereinafter the composition may be referred to as a "photocatalytic film
30 forming composition").

No particular limitations are imposed on the photocatalytic particles which may be employed, so long as they are excited by UV or visible light, to thereby generate conduction electrons and holes. Examples of the
35 photocatalytic particles include particles of tin oxide, zinc oxide, ferric oxide, tungsten trioxide, bismuth

trioxide, strontium titanate, and titanium dioxide.

Of these, titanium dioxide particles are preferred, as they are chemically stable. The photocatalytic particles may be titanium dioxide particles comprising a condensed phosphate on their surfaces. Preferably, titanium dioxide particles comprising a pyrophosphate on their surfaces are employed. The condensed phosphate may exist on their surface like island, like group islands, or like musk melon texture.

Any crystal form of rutile TiO_2 , anatase TiO_2 , and brookite TiO_2 may be used. A mixture of these crystal forms may also be used. Preferably, titanium dioxide which comprises brookite is employed, as they exhibit high photocatalytic activity. Of these, it is preferred that titanium dioxide which comprises brookite constitutes about 70 mass% or more on the basis of the total amount of the titanium dioxide.

The photocatalytic particles preferably have an average primary particle size of about $0.001\ \mu\text{m}$ to about $0.1\ \mu\text{m}$, more preferably about $0.001\ \mu\text{m}$ to about $0.08\ \mu\text{m}$. This is because, when the particle size exceeds about $0.1\ \mu\text{m}$, the resultant photocatalytic film exhibits poor transparency, whereas when the particle size is less than about $0.001\ \mu\text{m}$, productivity of the particles is considerably lowered. The average primary particle size is calculated from the BET specific surface area on the assumption that primary particles are true spheres.

The aluminum alkoxide hydrolysis-polycondensation product or aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product contained in the binder solution preferably assumes the form of particles having a size equal to or smaller than that of the photocatalytic particles. The powder obtained through drying of the binder solution at about 200°C preferably has a BET specific surface area of about $100\ \text{m}^2/\text{g}$ or more. This is because, when the powder has a BET

specific surface area of less than about 100 m²/g, adhesive strength is lowered, and difficulty is encountered in effecting exposure of the photocatalytic particles, leading to lowering of photocatalytic activity.

The aforementioned photocatalytic particles are mixed with the binder solution, and if desired, a hydrophilic organic solvent and water are mixed with the resultant mixture, to thereby prepare a photocatalytic film forming composition. The amount (solid content) of the photocatalytic particles in the photocatalytic film forming composition is preferably about 0.5 mass% to about 7 mass%. When the amount of the particles is less than about 0.5 mass%, a photocatalytic film formed through application of the composition becomes thin, and the film exhibits low photocatalytic effect. Therefore, in order to obtain the photocatalytic effect of the film, the process of application of the composition must be performed repeatedly. In contrast, when the amount of the particles exceeds about 7 mass%, the photocatalytic film forming composition exhibits poor storage stability, and the work life of the composition is shortened.

The amount of the aluminum alkoxide hydrolysis-polycondensation product, which is contained in the binder solution, in the photocatalytic film forming composition is preferably about 0.5 mass% to about 10 mass%, more preferably about 1 mass% to about 5 mass%, most preferably about 2 mass% to about 4 mass% as reduced to Al₂O₃; and the amount of the aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product, which is contained in the binder solution, in the photocatalytic film forming composition is preferably about 0.1 mass% to about 3 mass%, more preferably about 0.5 mass% to about 2.5 mass% as reduced to Al₂O₃, and about 0.1 mass% to about 1 mass%, more preferably about 0.2 mass% to about 0.8 mass% as reduced to TiO₂.

When the amount of the aluminum alkoxide hydrolysis-

polycondensation product is less than about 0.5 mass% as reduced to Al_2O_3 , adhesive strength between the photocatalytic particles and a substrate becomes insufficient, whereas when the amount of the product exceeds about 10 mass% as reduced to Al_2O_3 , the adhesive strength increases, but the photocatalytic activity is lowered. When the amount of the aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product is less than about 0.1 mass% as reduced to Al_2O_3 or TiO_2 , adhesive strength between the photocatalytic particles and a substrate becomes insufficient, whereas when the amount of the product exceeds about 3 mass% as reduced to Al_2O_3 or exceeds about 1 mass% as reduced to TiO_2 , the photocatalytic activity is lowered. In the aforementioned composition, the ratio by mass of the photocatalytic particles to the hydrolysis-polycondensation product (as reduced to Al_2O_3) is preferably about 14 : 1 to about 1 : 20, more preferably about 10:1 to about 1:10.

A dispersion which has been prepared by dispersing the photocatalytic particles in water may be employed in the photocatalytic film forming composition. The dispersion preferably has a pH of about 5 to about 8. In order to enhance applicability of the composition, an appropriate amount of water may further be incorporated into the composition.

Even when the amount of the hydrophilic organic solvent in the photocatalytic film forming composition is reduced to about 10 mass% or less, the composition exhibits sufficient photocatalytic activity and adhesive strength. However, in order to enhance applicability of the composition, an appropriate amount of a hydrophilic organic solvent may further be incorporated into the composition.

The above-prepared photocatalytic film forming composition has a pH of about 5 to about 8 (i.e., neutral), and thus can be applied to a variety of

substrates and materials of applicator. In addition, the composition enables improvement of the working environment.

From the viewpoint of applicability, the
5 photocatalytic film forming composition may further contain an appropriate amount of a surfactant. Examples of the surfactant which may be employed include condensed phosphates, lignin sulfonates, carboxymethyl cellulose, naphthalenesulfonate-formalin condensation products,
10 polyacrylates, acrylic acid-maleate copolymers, olefin-maleate copolymers, alkyl diphenyl ether disulfonates, and nonionic surfactants. Preferably, polyacrylic acid-based surfactants and polyoxyethylene alkyl ethers are employed.

15 When the photocatalytic film forming composition of the present invention is applied to a substrate such that a film formed through drying of the composition has a thickness of 200 nm, preferably, the total light transmittance of the resultant film is about 90% or more.
20 When the total light transmittance is lower than about 90%, the film exhibits poor transparency, and the transparency and design of the substrate are impaired.

The composite material of the present invention has a surface onto which the aforementioned photocatalytic
25 film forming composition is applied.

Application of the composition may be performed by means of a typical technique such as spin coating, spray coating, flow coating, dip coating, or bar coating. The thickness of the film is preferably about 0.01 μm to
30 about 3 μm , from the viewpoints of transparency and film strength. From the viewpoint of suppression of the interference color of the film, the thickness of the film is about 0.01 μm to about 0.3 μm , preferably about 0.8 μm to about 3 μm .

35 After being applied onto a substrate, the photocatalytic film forming composition is cured at about

10°C to about 40°C for at least about 24 hours, to
thereby form a photocatalytic film. The thus-formed film
has a hardness of about 2H or more as measured by means
of a pencil hardness test, and has adhesive strength
5 suitable for practical use. The pencil hardness test is
specified by JIS K-5400.

When a stronger photocatalytic film is required, the
photocatalytic film forming composition is applied onto a
substrate, and then cured at about 40°C to about 200°C
10 for about five minutes to about 24 hours. The higher the
curing temperature, the shorter the curing time. The
thus-formed film has a hardness of about 4H or more as
measured by means of the pencil hardness test.

When a composite material having the thus-formed
15 photocatalytic film is photoexcited such that the contact
angle between the film and water becomes about 10° or
less, and then the material is allowed to stand in the
dark for about 48 hours, the contact angle between the
film and water can be about 10° or less.

20 The film of the present invention exhibits excellent
durability in the use environment. Specifically, even
when the film is subjected to an acceleration-exposure
test employing a xenon lamp for about 5,000 hours, the
strength of the film is not lowered; i.e., the film is
25 suitable for practical use. The acceleration-exposure
test is specified by JIS K-5600.

Examples of the substrate to be employed include
substrates formed of glass, metal, concrete, ceramics,
stone, plaster board, and ceramic board. When the
30 composite material is applied to a plastic substrate or a
similar substrate, in order to prevent impairment of the
substrate by the photocatalytic effect, an inorganic hard
coat is provided on the substrate. Examples of the
inorganic hard coat include silica-based hard coats and
35 titania-based hard coats.

The substrate onto which the composite material is
applied is applicable to, for example, a material for an

exterior wall of a building, a soundproof wall for a road, a guardrail, a bridge structure, a windowpane of a building, a glass material for a building, a glass material for a showcase, a glass material for a fluorescent lamp, an advertising signboard, a transparent soundproof wall for a road, a transparent resin building material for exterior finishing, a filter for a deodorizing apparatus, a reactor for water treatment, an interior decoration tile, a water bath, a wall of a flowing-water channel, and a shade for a lighting apparatus.

EXAMPLES

The present invention will next be described in more detail by way of Examples, which should not be construed as limiting the invention.

[Example 1]

(Photocatalytic particles)

Ion exchange water (50 L), which had been weighed in advance, was heated to 98°C with stirring and maintained at this temperature. A titanium tetrachloride aqueous solution (Ti concentration: 15% by mass) (product of Sumitomo Titanium Corporation) (3.6 kg) was added dropwise to the heated water over 60 minutes. The thus-obtained white suspension was subjected to dialysis by use of an electric dialyzer, to thereby adjust the pH of the suspension to 4. Subsequently, the suspension was concentrated by use of an ultrafiltration membrane, to thereby yield a white slurry. A portion of the white slurry was collected, and the solid content was measured by means of the dry constant weight method and found to be 10 mass%. The resultant solid (dried powder) was subjected to structure analysis by use of an X-ray diffraction apparatus. As a result, the powder was found to be of brookite titanium dioxide. The titanium dioxide powder was found to have an average primary particle size of 0.04 μm as calculated from the BET specific surface area on the assumption that the primary particles are

true spheres.

(Binder solution)

Ion exchange water (9 L), methanol (3 L),
acetylacetone (500 g), and acetic acid (500 g) were fed
5 into a reaction container equipped with a reflux
condenser, and heated to 70°C with stirring and
maintained at this temperature. Aluminum triisopropoxide
(1.2 kg) was added to the resultant mixture, and refluxed
10 left to cool under stirring, to thereby yield a
hydrolysis-polycondensation product solution (binder
solution).

The kinematic viscosity of the resultant solution
was measured by use of a Canon-Fenske kinematic
15 viscometer (product of Shibata Scientific Technology,
Ltd.), and was found to be 2.1×10^{-6} m²/s. The pH of the
solution was found to be 5. After the solution was
stored at room temperature (20°C) for three months, the
kinematic viscosity of the solution was measured, and as
20 a result, the kinematic viscosity was found to be
maintained at 2.0×10^{-6} m²/s. In addition, the solution
did not produce precipitates, and was stable.

The solution was applied to a glass slide (Micro
Slide Glass S7213, product of Matsunami Glass Ind., Ltd.)
25 by means of spin coating, and dried and cured at 20°C for
24 hours. The thickness of the resultant film was
measured by use of a contact-type surface roughness meter
(Surfcorder SE-30D, product of Kosaka Laboratory Ltd.),
and found to be 0.2 μm. The untreated glass slide and
30 the glass slide coated with the aluminum compound film
were subjected to measurement of total light
transmittance by use of a haze meter (TC-HIIIDPK, product
of Tokyo Denshoku Co. Ltd), and the total light
transmittance of the film formed on the glass slide was
35 calculated on the basis of the total light transmittance
of the untreated glass slide (taken as 100%). As a

result, the total light transmittance of the film was found to be 99%, and the haze thereof was found to be 0.1%. Meanwhile, the above-obtained solution was dried at 200°C, to thereby yield a hydrolysis-polycondensation product. The BET specific surface area of the product was measured, and found to be 120 m²/g.

(Photocatalytic film forming composition)

The above-obtained titanium dioxide slurry (200 g), ion exchange water (500 g), and the binder solution (300 g) were mixed together, to thereby prepare a photocatalytic film forming composition. The composition was found to have a pH of 6. The composition was applied to the aforementioned glass slide, and dried and cured at 20°C for 24 hours. The thickness of the resultant photocatalytic film was measured, and found to be 200 nm. The total light transmittance of the photocatalytic film was measured in a manner similar to that for the case of the film formed from the binder solution. As a result, the total light transmittance and haze of the photocatalytic film were found to be 91% and 0.5%, respectively. The photocatalytic film was subjected to the pencil hardness test, and the film was found to have a hardness of 3H. After the film-coated glass slide was subjected to the acceleration-exposure test employing a xenon lamp for 5,000 hours, the film was subjected to the pencil hardness test. As a result, the film was found to have a hardness of 3H. The hydrophilicity of the film was evaluated on the basis of the contact angle between the surface layer of the film and a water droplet on the surface layer. For evaluation of the hydrophilicity, the photocatalytic film was exposed to light sufficiently, and then allowed to stand in the dark for 48 hours, followed by measurement of the contact angle. The contact angle was measured by use of a contact angle meter (CA-D, product of Kyowa Interface Science Co., Ltd.). As a result, the contact angle was found to be 6°.

[Example 2]

In a manner similar to that of Example 1, ion exchange water (50 L), which had been weighed in advance, was heated to 98°C with stirring and maintained at this temperature. A titanium tetrachloride aqueous solution (Ti concentration: 15% by mass) (product of Sumitomo Titanium Corporation) (3.6 kg) was added dropwise to the heated water over 60 minutes. The thus-obtained white suspension was subjected to dialysis by use of an electric dialyzer, to thereby adjust the pH of the suspension to 4.

Subsequently, sodium pyrophosphate (for food addition, product of Taihei Chemical Industrial Co., Ltd.) (0.1 kg) was added to the resultant titanium dioxide slurry, which was stirred sufficiently until the pyrophosphate was dispersed in the slurry. Thereafter, calcium chloride (for food addition, product of Tokuyama Corporation) (200 g) was added to pure water (2,000 L) which had been weighed in advance, to thereby prepare a calcium chloride solution. The above-obtained sodium-pyrophosphate-containing titanium dioxide slurry and the calcium chloride solution were mixed together, and the resultant mixture was maintained at 40°C for four hours. The electrical conductivity of the mixture was found to be 10,000 $\mu\text{S}/\text{cm}$.

Subsequently, the resultant slurry was washed through filtration by use of a rotary filter press (product of Kotobuki Engineering & Manufacturing Co., Ltd.), and then washed thoroughly with water until the electrical conductivity of the filtrate became 50 $\mu\text{S}/\text{cm}$, to thereby yield a photocatalytic-particle-containing slurry. The solid content and pH of the resultant slurry were found to be 10 mass% and 8, respectively. The photocatalytic particles were found to have an average primary particle size of 0.06 μm .

In a manner similar to that of Example 1, the

aforementioned photocatalytic particles were mixed with the binder solution of Example 1, to thereby prepare a photocatalytic film forming composition. The composition was applied to a glass slide, and cured at 20°C for 24 hours.

Characteristics of the composition and the resultant film were evaluated. The results are shown in Table 1. [Example 3]

In a manner similar to that of Example 1, ion exchange water (50 L), which had been weighed in advance, was heated to 98°C with stirring and maintained at this temperature. A titanium tetrachloride aqueous solution (Ti concentration: 15% by mass) (product of Sumitomo Titanium Corporation) (3.6 kg) was added dropwise to the heated water over 60 minutes. The thus-obtained white suspension was subjected to dialysis by use of an electric dialyzer, to thereby adjust the pH of the suspension to 4.

Subsequently, sodium pyrophosphate (0.1 kg) was added to the resultant titanium dioxide slurry, which was stirred sufficiently until the pyrophosphate was dispersed in the slurry. Thereafter, the resultant slurry was washed through filtration by use of a rotary filter press, to thereby yield a photocatalytic-particles-containing slurry. The solid content and pH of the resultant slurry were found to be 10 mass% and 8, respectively. The photocatalytic particles were found to have an average primary particle size of 0.02 μm .

In a manner similar to that of Example 1, the aforementioned photocatalytic particles were mixed with the binder solution of Example 1, to thereby prepare a photocatalytic film forming composition. The composition was applied to a glass slide, and cured at 20°C for 24 hours.

Characteristics of the composition and the resultant film were evaluated. The results are shown in Table 1. (Photocatalytic activity)

Catalytic activity of the photocatalytic film was evaluated through the following procedure.

The photocatalytic film was formed on a glass plate (size: 20 cm x 20 cm) such that the thickness of the film was 0.2 μm . The glass plate with the film was placed in a Tedlar Bag (registered trademark) (capacity: 5 L), and dry air containing 60 ppm hydrogen sulfide was fed into the bag, followed by sealing. The glass plate with the film was irradiated with UV rays of 365 nm (intensity: 0.5 mW/cm²) by use of a blacklight (Blacklight Blue Fluorescent Lamp FL20SBL-B, product of Matsushita Electric Industrial Co., Ltd.).

One hour after the irradiation, the concentration of the hydrogen sulfide was measured by use of a gas detector tube (No. 4LL, product of Gastec Corporation). In this measurement, no hydrogen sulfide was detected. [Example 4]

Ion exchange water (9 L), methanol (3 L), acetylacetone (500 g), and acetic acid (300 g) were fed into a reaction container equipped with a reflux condenser, and heated to 70°C with stirring and maintained at this temperature. Aluminum triisopropoxide (0.8 kg) was added to the resultant mixture, and refluxed for two hours, to thereby yield a binder solution. In a manner similar to that described above, the binder solution was mixed with the photocatalytic particles of Example 1, to thereby prepare a photocatalytic film forming composition. The composition was applied to a glass slide, and cured at 30°C for 24 hours, to thereby form a film. Characteristics of the binder solution, composition, and film were evaluated. The results are shown in Table 1.

[Example 5]

Ion exchange water (9 L), methanol (3 L), acetylacetone (500 g), and acetic acid (500 g) were fed into a reaction container equipped with a reflux

condenser, and heated to 70°C with stirring and maintained at this temperature. Aluminum trimethoxide (0.8 kg) was added to the resultant mixture, and refluxed for two hours, to thereby yield a binder solution. In a manner similar to that described above, the binder solution was mixed with the photocatalytic particles of Example 3, to thereby prepare a photocatalytic film forming composition. The composition was applied to a glass slide, and cured at 30°C for 24 hours, to thereby form a film. Characteristics of the binder solution, composition, and film were evaluated. The results are shown in Table 1.

[Example 6]

Ion exchange water (9 L), methanol (3 L), acetylacetone (500 g), and 60% nitric acid (300 g) were fed into a reaction container equipped with a reflux condenser, and heated to 70°C with stirring and maintained at this temperature. Aluminum triisopropoxide (0.8 kg) was added to the resultant mixture, and refluxed for two hours, to thereby yield a binder solution. In a manner similar to that described above, the binder solution was mixed with the photocatalytic particles of Example 3, to thereby prepare a photocatalytic film forming composition. The composition was applied to a glass slide, and cured at 40°C for 24 hours, to thereby form a film. Characteristics of the binder solution, composition, and film were evaluated. The results are shown in Table 1.

[Example 7]

The procedure of Example 5 was repeated, except that the amount of methanol was changed to 4 L, and aluminum triisopropoxide (1.6 kg) was employed instead of aluminum trimethoxide (0.8 kg), to thereby form a film. Characteristics of the resultant binder solution, composition, and film were evaluated. The results are shown in Table 1.

[Example 8]

The procedure of Example 5 was repeated, except that aluminum tri-sec-butoxide (1.6 kg) was employed instead of aluminum trimethoxide (0.8 kg), and butanol (6 L) was employed instead of methanol (3 L), to thereby form a film. Characteristics of the resultant binder solution, composition, and film were evaluated. The results are shown in Table 1.

[Example 9]

Methanol (1.5 L), acetylacetone (70 g), ion exchange water (30 g), 60% nitric acid (10 g), and acetic acid (20 g) were fed into a reaction container equipped with a reflux condenser, and heated to 40°C with stirring and maintained at this temperature. Aluminum trimethoxide (50 g) was added to the resultant mixture, and refluxed for one hour. Subsequently, titanium tetraisopropoxide (20 g) was added to the resultant mixture, and refluxed for one hour, to thereby yield a binder solution. In a manner similar to that described above, the binder solution was mixed with the photocatalytic particles of Example 3, to thereby prepare a photocatalytic film forming composition. The composition was applied to a glass slide, and cured at 40°C for 24 hours, to thereby form a film. Characteristics of the binder solution, composition, and film were evaluated. The results are shown in Table 1.

[Example 10]

Methanol (1.5 L), acetylacetone (50 g), ion exchange water (30 g), and 60% nitric acid (10 g) were fed into a reaction container equipped with a reflux condenser, and heated to 40°C with stirring and maintained at this temperature. Aluminum triisopropoxide (80 g) was added to the resultant mixture, and refluxed for one hour. Subsequently, titanium tetraisopropoxide (20 g), acetic acid (20 g), and acetylacetone (20 g) were added to the resultant mixture, and refluxed for one hour, to thereby yield a binder solution. In a manner similar to that described above, the binder solution was mixed with the

photocatalytic particles of Example 3, to thereby prepare a photocatalytic film forming composition. The composition was applied to a glass slide, and cured at 40°C for 24 hours, to thereby form a film.

5 Characteristics of the binder solution, composition, and film were evaluated. The results are shown in Table 1.
[Example 11]

The procedure of Example 10 was repeated, except that the amount of ion exchange water was changed from 30
10 g to 120 g, to thereby form a film. Characteristics of the resultant binder solution, composition, and film were evaluated. The results are shown in Table 1.
[Example 12]

The procedure of Example 10 was repeated, except
15 that aluminum tri-n-butoxide was employed instead of aluminum triisopropoxide, to thereby form a film. Characteristics of the resultant binder solution, composition, and film were evaluated. The results are shown in Table 1.
20 [Comparative Example 1]

Tetraethoxysilane (40 g) and methanol (200 g) were fed into a reaction container equipped with a reflux condenser, and mixed together. Subsequently, ion exchange water (50 g) employed for hydrolysis, and 60%
25 nitric acid (1.5 g) serving as an acid catalyst were added to the resultant mixture, and the mixture was maintained at 40°C, to thereby allow hydrolysis to proceed for five hours. The pH of the resultant hydrolysis solution was measured, and found to be 1.5.

30 When the thus-obtained ethyl silicate hydrolysis binder solution (5 g) was mixed with the titanium dioxide slurry employed in Example 3 (2 g) and ion exchange water (3 g), considerable aggregation was observed in the resultant mixture. The pH of the mixture was found to be
35 4. The mixture was applied to a glass plate, and the total light transmittance of the resultant film was measured. As a result, the total light transmittance was

found to be 55%. The photocatalytic activity of the film was evaluated in a manner similar to that of Example 3, and as a result, the concentration of hydrogen sulfide was found to be 35 ppm after one-hour irradiation of the film with light; i.e., the film exhibited poor photocatalytic activity. A film formed through drying of the above mixture at 20°C for 24 hours was subjected to the pencil hardness test, and as a result, the film was found to have a hardness of H or less.

10 [Comparative Example 2]

Zirconium tetrabutoxide (25 g), isopropyl alcohol (5 g), and methanol (1 g) were fed into a container equipped with a reflux condenser, and stirred. Subsequently, the titanium dioxide slurry employed in Example 1 (25 g) was added to the resultant mixture, and stirred. Although the pH of the resultant mixture was found to be 6, aggregation of titanium oxide was observed in the mixture. The mixture was applied to a glass plate, and the total light transmittance of the resultant film was measured. As a result, the total light transmittance was found to be 41%. A film formed through drying of the above mixture at 20°C for 24 hours was subjected to the pencil hardness test, and as a result, the film was found to have a hardness of H or less.

25 [Comparative Examples 3 through 6]

The procedure of Example 1 was repeated, except that the composition of a binder solution was changed as shown in Table 2, to thereby form a film. Characteristics of the resultant binder solution, composition, and film were evaluated. The results are shown in Table 3.

Table 1

Ex.	Binder solution					Photocatalytic film forming composition		Photocatalytic film			
	Total light transmittance (%)	Haze (%)	Specific surface area after drying at 200°C (m ² /g)	Kinematic viscosity (× 10 ⁻⁶ m ² /s)	Kinematic viscosity after storage at 20°C for 3 months (× 10 ⁻⁶ m ² /s)	pH	Amount of hydrophilic organic solvent (mass%)	Total light transmittance (%)	Haze (%)	Contact angle after being placed in the dark for 48 hours (°)	Pencil hardness value after exposure test
1	99	0.1	120	2.1	2.0	5	12	91	0.5	6	3H
2	99	0.1	120	2.1	2.0	7	12	92	0.2	5	3H
3	99	0.1	120	2.1	2.0	7	12	93	0.4	7	3H
4	97	0.3	110	1.8	1.7	6	12	92	0.3	5	3H
5	95	0.8	130	2.3	2.1	7	12	90	0.8	9	3H
6	96	0.6	140	2.0	1.9	6	12	91	0.5	4	3H
7	99	0.1	110	1.9	1.9	7	12	95	0.1	6	3H
8	95	0.7	150	2.9	2.7	7	14	90	0.8	9	3H
9	96	0.3	105	1.1	1.1	5	27	91	0.7	10	3H
10	97	0.1	120	1.0	1.1	5	27	90	0.5	10	3H
11	95	0.3	110	1.6	1.8	5	26	91	0.5	10	3H
12	95	0.4	120	1.8	1.9	5	27	90	0.7	10	3H

Table 2

	Comparative Example			
	3	4	5	6
Ion exchange water	20 L	1 L	10 L	10 L
Methanol	0 L	10 L	10 L	10 L
Acetylacetone	500 g	500 g	0 g	500 g
Acetic acid	500 g	500 g	500 g	0 g
Aluminum isopropoxide	1.2 kg	1.2 kg	1.2 kg	1.2 kg

Table 3

Comp. Ex.	Binder solution					Photocatalytic film forming composition		Photocatalytic film			
	Total light transmittance (%)	Haze (%)	Specific surface area after drying at 200°C (m ² /g)	Kinematic viscosity (cSt)	Kinematic viscosity after storage at 20°C for 3 months (cSt)	pH	Amount of hydrophilic organic solvent (mass%)	Total light transmittance (%)	Haze (%)	Contact angle after being placed in the dark for 48 hours (°)	Pencil hardness value after exposure test
3	85	1.2	110	1.8	1.5	7	5 or less	77	22	22	Exfoliation
4	91	0.8	120	2.6	2.0	7	21	88	11	12	H
5	95	0.7	70	1.8	Precipitates	7	12	85	14	33	H
6	98	0.3	20	1.2	1.2	8	12	55	30	40	Exfoliation

Industrial Applicability

The aluminum alkoxide hydrolysis-polycondensation product solution of the present invention enables, without heating, formation of a transparent and highly durable film on the surface of various substrates, and can be reliably stored in a hermetic manner at ambient temperature over a long period of time.

The film forming composition formed from the solution is very stable, and the solution can be effectively employed as a binder for photocatalytic particles.

From a photocatalytic film forming composition containing the aforementioned solution and photocatalytic particles, there is readily formed a transparent film which has high hardness, which is barely impaired by light, and which exhibits, through photoexcitation of the photocatalytic particles, deodorization, antifouling, hydrophilic, and antibacterial effects. Therefore, the composition is applicable to the surface of various substrates.

CLAIMS

1. A hydrolysis polycondensation product solution, comprising a hydrolysis-polycondensation product of an aluminum alkoxide represented by the formula Al(OR)_3 ,
5 (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and
10 imino); an alcohol; and water, which composition cures within about 24 hours at a temperature of about 10 to about 40°C, to thereby form a transparent film.

2. A hydrolysis polycondensation product solution, comprising a cohydrolysis-polycondensation product of an
15 aluminum alkoxide represented by the formula Al(OR)_3 , (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl,
20 ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino) and a titanium alkoxide represented by the formula Ti(OR')_4 , (wherein R' represents a substituted or unsubstituted, strait or branched, saturated or
25 unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino); an alcohol; and water, which
composition cures within about 24 hours at a temperature of about 10 to about 40°C, to thereby form a transparent
30 film.

3. A hydrolysis polycondensation product solution according to claim 1 or 2, comprising β -diketone.

4. An aluminum alkoxide hydrolysis-polycondensation product solution comprising an aluminum
35 alkoxide represented by the formula Al(OR)_3 , (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-

ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino), a β -diketone, an acid, water, and an alcohol in proportions by mol of about 1 : about 0.1 to about 3 : about 0.5 to about 2 : at least about 30 : about 10 to about 20.

5 5. An aluminum alkoxide hydrolysis-polycondensation product solution comprising an aluminum alkoxide represented by the formula Al(OR)_3 (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino), a titanium
10 alkoxide, a β -diketone, an acid, water, and an alcohol in proportions by mol of about 1 : about 0.01 to about 0.5 : about 0.1 to about 3 : about 0.5 to about 2 : about 1 to about 20 : about 80 to about 140.

15 6. A hydrolysis-polycondensation product solution according to any one of claims 3 to 5, wherein the β -diketone is acetylacetone, the acid is acetic acid, and the alcohol is methanol.

20 7. A hydrolysis-polycondensation product solution according to claim 4, which has a kinematic viscosity of about 1.5×10^{-6} to about $3.0 \times 10^{-6} \text{ m}^2/\text{s}$.

25 8. A hydrolysis-polycondensation product solution according to claim 5, which has a kinematic viscosity of about 0.5×10^{-6} to about $2.0 \times 10^{-6} \text{ m}^2/\text{s}$.

30 9. A hydrolysis-polycondensation product solution according to any one of claims 1 through 8, which, when hermetically stored at about 20°C for about 90 days, undergoes no change in kinematic viscosity, and which, even when mixed with photocatalytic particles, does not cohesion of the particles.

35 10. A hydrolysis-polycondensation product solution

according to any one of claims 1 through 9, wherein a powder formed through drying of the hydrolysis-polycondensation product solution at about 200°C has a specific surface area of at least about 100 m²/g.

5 11. A hydrolysis-polycondensation product solution according to any one of claim 1 to claim 10, wherein, when a film is formed through drying of the hydrolysis-polycondensation product solution at about 40°C so as to have a thickness of about 200 nm, the film has a total
10 light transmittance of at least about 95% and a haze of about 1% or less.

 12. A method for producing an aluminum alkoxide hydrolysis polycondensation product solution, comprising adding an aluminum alkoxide represented by the formula
15 Al(OR)₃ (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido, sulfinyl,
20 sulfonyl and imino) in an amount of about 1 mole part into a mixed solution of about 0.1 to about 3 mole parts of β-diketone, about 0.5 to about 2 mole parts of an acid and about 10 to about 20 mole parts of an alcohol; adding about 30 mole parts or more of water to the solution, per
25 1 mole part of the aluminum alkoxide; and heating the solution to a temperature of about 40 to about 70°C.

 13. A method for producing an aluminum alkoxide-titanium alkoxide cohydrolysis polycondensation product solution, comprising adding an aluminum alkoxide
30 represented by the formula Al(OR)₃ (wherein R represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected from carbonyl, ether, ester, amido, sulfido,
35 sulfinyl, sulfonyl and imino) in an amount of about 1 mole part into a mixed solution of about 0.1 to about 3

mole parts of β -diketone, about 0.5 to about 2 mole parts of an acid, about 80 to about 140 mole parts of an alcohol and about 1 to about 20 mole parts of water; and adding to the solution about 0.01 to about 0.5 mole part
5 of a titanium alkoxide represented by the formula $Ti(OR')_3$ (wherein R' represents a substituted or unsubstituted, strait or branched, saturated or unsaturated, alkyl group, alkyl-ester group or aryl group, which may optionally contain at least one selected
10 from carbonyl, ether, ester, amido, sulfido, sulfinyl, sulfonyl and imino), per 1 mole part of the aluminum alkoxide, while heating the solution to a temperature of about 40 to about 70°C.

14. A composition for forming a photocatalytic film, comprising the hydrolysis-polycondensation product solution as recited in claims 1 through 11, and photocatalytic particles exhibiting, through photoexcitation, deodorization, antifouling, hydrophilic, and antibacterial effects.

20 15. A composition for forming a photocatalytic film according to claim 14, wherein the solid content of the photocatalytic particles is about 0.5 mass% to about 7 mass%, and the amount of the hydrolysis-polycondensation product of an aluminum alkoxide represented by the
25 formula $Al(OR)_3$ is about 0.5 mass% to about 10 mass% as reduced to Al_2O_3 .

16. A composition for forming a photocatalytic film according to claim 14, wherein the solid content of the photocatalytic particles is about 0.5 mass% to about 7
30 mass%, and the amount of the aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product is about 0.1 mass% to about 3 mass% as reduced to Al_2O_3 and about 0.1 mass% to about 1 mass% as reduced to TiO_2 .

17. A composition for forming a photocatalytic film
35 according to any one of claims 14 through 16, wherein the photocatalytic particles have an average particle size of

about 0.001 to about 0.1 μm as calculated from the BET specific surface area.

18. A composition for forming a photocatalytic film according to any one of claims 14 through 17, wherein the
5 photocatalytic particles contain at least one species selected from the group consisting of titanium dioxide particles and titanium dioxide particles having a condensed phosphate on their surfaces.

19. A composition for forming a photocatalytic film
10 according to claim 18, wherein the titanium dioxide particles contain at least one crystal form selected from the group consisting of rutile, anatase, and brookite.

20. A composition for forming a photocatalytic film according to any one of claims 14 through 19, wherein the
15 content of the alcohol is about 30 mass% or less.

21. A composition for forming a photocatalytic film according to any one of claims 14 through 20, which has a pH of about 5 to about 8.

22. A composite material comprising a film
20 exhibiting, through photoexcitation, deodorization, antifouling, hydrophilic, and antibacterial effects, the film being formed from a composition for forming a photocatalytic film, the composition containing an aluminum alkoxide hydrolysis-polycondensation product
25 solution or an aluminum alkoxide-titanium alkoxide cohydrolysis-polycondensation product solution and photocatalytic particles.

23. A composite material according to claim 22, wherein the photocatalytic particles are at least one
30 species selected from the group consisting of titanium dioxide particles and titanium dioxide particles having a condensed phosphate on their surfaces.

24. A composite material according to claim 23, wherein the titanium dioxide particles contain at least
35 one crystal form selected from the group consisting of rutile, anatase, and brookite.

25. A composite material according to any one of

claims 22 through 24, wherein, after the material is photoexcited such that the contact angle between the film and water becomes about 10° or less, and then the material is allowed to stand in the dark for about 48
5 hours, the contact angle between the film and water is about 10° or less.

26. A composite material according to any one of claims 22 through 25, wherein, after the material is subjected to an acceleration-exposure test employing a
10 xenon lamp for about 5,000 hours, the film has a pencil hardness value of at least about 2H.

27. A composite material according to any one of claims 22 through 26, wherein, when the thickness of the film is about 200 nm, the film has a total light
15 transmittance of at least about 90% and a haze of about 1% or less.

28. A material for an exterior wall of a building, a soundproof wall for a road, a windowpane of a building, a glass material for a showcase, a glass material for a
20 fluorescent lamp, a guardrail, a filter for a deodorizing apparatus, a reactor for water treatment, an interior decoration tile, a water bath, or a shade for a lighting apparatus, comprising a composite material as recited in any one of claims 22 through 27.

25 29. An advertising signboard, a transparent soundproof wall for a road, a transparent resin building material for exterior finishing, or a shade for a lighting apparatus, comprising a hard coat layer containing a composite material as recited in any one of
30 claims 22 through 28.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/10085

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G79/10 C01F7/36 C23C18/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C01F C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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P document published prior to the international filing date but later than the priority date claimed

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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